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The phonon density of states of α- and δ-plutonium by inelastic x-ray scattering

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Inelastic x-ray scattering measurements of the phonon density of states (DOS) were performed on polycrystalline samples of pure α-Pu and δ-$Pu_{0.98}Ga_{0.02}$ at room temperature. The heat capacity of α-Pu is well reproduced by contributions calculated from the measured phonon DOS plus conventional thermal expansion and electronic contributions, showing that α-Pu is a 'well-behaved' metal in this regard. A comparison of the phonon DOS of the two phases at room temperature surprised us in that the vibrational entropy difference between them is only a quarter of the total entropy difference expected from known thermodynamic measurements. The missing entropy is too large to be accounted for by conventional electronic entropy and evidence from the literature rules out a contribution from spin fluctuations. Possible alternative sources for the missing entropy are discussed.

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Of the six unique solid-state modifications of plutonium, the ground state (α-phase, monoclinic symmetry) displays the lowest symmetry for a metal in the periodic chart. This low-symmetry ground state, combined with complex intrinsic properties, restricts an extrapolation from surrogate metallic systems. For example, some of the phases differ in density up to 30 % at ambient pressure [1]. Many theories have been put forth to explain all these changes, most having to do with Pu's 5*f* electrons being on the edge of localization [2, 3]. For example, it has been argued that electron spin fluctuations are present in Pu and that the fcc δ–phase might be stabilized with respect to the lower temperature phases by spin-fluctuation entropy associated with *f*-electron localization [4, 5]. This idea is similar to what is known to happen with cerium's $\alpha \rightarrow \gamma$ volume-collapse transition [6, 7], only unlike cerium, experiments have failed to detect local magnetic moments (static or dynamic) in δ–Pu [8, 9]. Another set of proposals, which are more phenomenological, assumes a mixture of local electronic states for the Pu atoms in the δ–phase, each with a different energy and effective atomic size [10, 11]. This idea has shown some success in explaining anomalies in the thermal expansion of δ-Pu by assuming a two state Invar-like model [11]. From this model entropy follows from the mixture of local electronic states that would tend to stabilize δ-phase with respect to the α-phase ground state with increasing temperature.

To critically evaluate these ideas it is important to quantify all the entropic contributions to these solid-state phase transitions. Phonons carry most of the entropy in solids at high temperatures and are therefore expected to play an important role. Measurements of the δ–phase phonon dispersion curves using x-rays [12], and phonon density of states (DOS) using neutrons [13], have been reported, but no measurements exist for phonons of the α–phase. Measurements of the heat capacity have also indicated a strong enhancement of the electronic contribution at low temperatures in the δ–phase, but not in the α–phase [14], hinting at the possibility of a significant change in the

electronic-correlation entropy at the transition [14]. Here we report inelastic x-ray scattering measurements of the phonon DOS of pure α–Pu and δ–$Pu_{0.98}Ga_{0.02}$, along with the heat capacity of pure α–Pu measured from 2 to 300 K. The heat capacity of the α–phase is mostly accounted for by the phonon contribution calculated from the DOS; the remainder is split almost equally between the volume expansion and electronic contribution extrapolated from low temperatures. This result contrasts with the observations in δ–Pu showing an enhanced electronic heat capacity at low temperatures [14] and emphasizes the importance of electronic correlations. The vibrational entropy difference between the two phases makes up only a small fraction of the total entropy difference.

The standard approach for measuring the phonon DOS is to collect neutron scattering spectra from a polycrystalline sample over a wide range of momentum transfers (Q). This approach has been successfully applied to determine the phonon DOS of δ^{242}Pu [13]. However, this measurement requires a large quantity of an isotope that is difficult to obtain in high purity, thus impeding further neutron work on Pu metal. Here we circumvent the isotope problem by using inelastic x-ray scattering [15] with the HERIX instrument at the Advanced Photon Source of Argonne National Laboratory. The 23.8 keV beam was used unfocused to allow sampling of approximately 1000 grains in our polycrystalline material, ensuring a powder average. Eight equally spaced analyzer crystals were positioned at a series of overlapping angles completely covering momentum transfers from Q = 2 to 7 $Å^{-1}$, yielding an average over several Brillouin Zones. The signal from each detector was normalized by the detector efficiency and the data was summed over all angles and detectors. The phonon DOS was extracted from the resulting spectra by subtracting the elastic peak and the incoherent multiphonon scattering determined iteratively [16-18], and then dividing out the thermal occupation and Debye-Waller factors. The validity of this approach with x-rays, which is essentially

identical to the established neutron approach, has been proven accurate with measurements of the phonon DOS of both diamond and MgO [18].

The heat capacity of pure α-Pu was measured using the thermal relaxation method in a Quantum Design PPMS [14, 19]. From 10 to 300 K, samples ranging from 20 to 30 mg were used while below 10 K sample masses of 5 to 10 mg were used. Samples were secured to the puck using Apiezon N-grease, ensuring good thermal contact. Immediately before each sample was studied, the addenda (puck and grease) were measured over the same T range. The heat capacity of the sample was determined by subtracting the addenda contribution from the raw data; systematic errors due to inaccuracies in the PPMS [19] and measurement of the sample masses were 1.5%. However additional errors due to self-heating were determined by a set of experiments on a heater of known input power. This resulted in an additional 3.5% error on the heat capacity.

The phonon DOS for δ–$Pu_{0.98}Ga_{0.02}$ (top panel) and pure α–Pu (bottom panel) are shown in Fig. 1. The δ-phase sample used in the present measurement came from the same batch of material used by Wong *et al.* for measuring the phonon dispersion curves [12]. Nevertheless, the phonon DOS deduced from the force constant model fit to the phonon dispersion curves by Wong *et al.* (solid line in top panel) shows a significant difference with the measured phonon DOS (circles in top panel); the central feature around 6 meV associated with a transverse branch is about 1 meV higher in energy (stiffer) in the present phonon DOS measurement. The other features, including the upper longitudinal mode and phonon cutoff energy, are in reasonably good agreement with the measurements of Wong *et al.* [12]. Interestingly, this somewhat stiffer central feature is more in line with phonon dispersion results calculated using Dynamic Mean Field Theory [19]. The phonon DOS measured in δ-Pu using inelastic neutron scattering also show this feature at a higher energy, although the sample used was alloyed with a significant amount of Al [13]. The lower energy for the

transverse mode in the measurements by Wong *et al.* [12] may have been caused by a local residual shear strain on the single grain measured in the focused x-ray measurements. The phonon DOS measurement presented here is from over ~1000 grains, which averages out effects of a local residual strain.

The pure α-phase phonon DOS (circles in bottom panel of Fig. 1) shows several features indicating nearly flat regions in the dispersion curves at 6, 8.8, 11.5, and 13.5 meV. A pronounced cutoff in phonon density occurs near 14.5 meV. Additional weaker intensity appears above 14.5 meV ending around 18 meV. The α-phase phonon DOS is stiffer than the δ-phase, as expected given its higher density. However, in terms of vibrational entropy, this stiffening only amounts to about (0.36±0.01) k_B/(Pu atom), a small fraction of the total entropy change of 1.3 k_B/(Pu atom) expected from the $\alpha \rightarrow \delta$ phase transition [21].

The heat capacity measured on a pure α-Pu sample along with the standard contributions from phonons, volume expansion, and electronic excitations is shown in Fig. 2. The constant volume contribution from the phonons was calculated from the phonon DOS using,

$$C_V^{ph}(T) = \frac{\partial}{\partial T}\left[\int_0^\infty \varepsilon g(\varepsilon) n(\varepsilon, T) d\varepsilon\right] \quad (1)$$

where $g(\varepsilon)$ is the phonon DOS and $n(\varepsilon, T)$ is the Bose-Einstein thermal occupation factor. The contribution from thermal expansion, C_P-$C_V = 9B\nu\alpha^2 T$, was calculated using standard values for the linear thermal expansion coefficient, α = 54x10^{-6}/K, bulk modulus, B = 55 GPa, and specific volume, ν = 0.0503 cm^3/g [22]. In addition, the thermal expansion coefficient was assumed to decrease rapidly at low temperatures in proportion to the phonon heat capacity calculated from Eq. (1); this behavior is expected for anharmonic phonon-driven thermal expansion [23]. The electronic contribution was determined from the low temperature fit of the linear electronic term determined by

Lashley *et al.* [14], where $\gamma(=C_{el}/T)$ is 17 mJ K^{-2} mol^{-2}. The measured heat capacity is in good agreement with the sum of the calculated contributions over most of the temperature range. The only exception is between 50 and 200 K where the measurement is slightly lower than the calculation. A modest lowering of the heat capacity is this range is expected for polycrystalline materials composed of grains with anisotropic thermal expansion, such as with α-Pu [24]. A build up of strain energy in the microstructure occurs on cooling owing to an incompatibility of the thermal expansions of individual grains that are bound together in the polycrystalline material; the release of this stored energy on heating lowers the observed heat capacity [24]. At very low temperatures this effect becomes small because the thermal expansion coefficient decreases with phonon depopulation, thus decreasing the energy release rate with temperature. At high temperatures the effect becomes small again because of thermal relaxation of the strains [25]. Hence, unlike with the heat capacity of δ-Pu [14], there are no unexpected anomalies in the α-Pu heat capacity and it is well reproduced using the measured phonon DOS.

The relatively small difference in vibrational entropy between the α and δ phases of plutonium is reminiscent of the small change that occurs during the $\gamma \rightarrow \alpha$ volume collapse transition in cerium [6], which can be described solely in terms of changes in the spin fluctuation entropy [7]. A similar magnetic stabilization in plutonium would not be surprising given its position on the periodic table [26], but experimental evidence shows that there are no detectable local moments in δ-Pu [8,9]. Furthermore, the lack of local moments δ-Pu has recently been explained theoretically in terms of electron coherence using Dynamic Mean Field Theory [27]. Thus, although the entropic contributions stabilizing the δ-phase with respect to the α-phase ground state cannot be conventional vibrations, they also cannot be accounted for by spin entropy. Electronic entropy from excitations across the Fermi level is another possible factor, but the primary difference between the phases

comes from an enhancement of the electronic contribution in δ-phase at temperatures below 25 K (see Fig. 2 in Ref [14] and note that the feature at 60 K is ascribed to the $\delta \rightarrow \alpha'$ phase transition). The extra entropy implied by this low temperature contribution makes up only about 10-20% of the 1.3 k_B/(Pu atom) of the transition entropy. The electronic contribution in δ-phase falls quickly down to near 17 mJ/mol-K (at 300 K), the value in α-phase, minimizing any difference at high temperatures. A third possible contributing factor could be dynamic nonlinear localization. Dynamic nonlinear localization can cause intrinsic localized vibrational modes that generate entropy by becoming activated randomly on the lattice at high temperatures [28]. Intrinsic local modes (ILMs) and their associated entropy have been reported for α-uranium at temperatures above 450 K [29]. However, ILMs and ordinary point defects are limited in the amount of entropy that they can contribute. In order to explain the remaining entropy essentially every other atom would have to become a "defect" resulting in a maximum configurational entropy of 0.69 k_B/atom, which would still be short of what is needed to account for the remaining ~0.8 k_B/atom. The fourth possible contribution is from a softening of the δ-phase phonons at high temperatures. A large intrinsic softening of the lattice vibrations at high temperatures has been observed in many of the light actinides, including α-U [29] and δ-Pu [31]. It has been argued that this effect results from thermal changes is the electronic structure rather than from conventional anharmonic phonon softening [32]. This unconventional softening (nonlinearity) entropy is large in δ-Pu since the Debye temperature has been shown to soften by 14% between 300 K and 593 K (the temperature where δ-phase becomes stable in pure material [21]). This provides another 0.4 k_B/(Pu atom), another component making up only a fraction of the 1.3 kB/(Pu atom) for the transition. Thus, the entropy driving the transition is likely a mix of unconventional sources.

In conclusion, the heat capacity of α-Pu is well described in terms of the measured phonons and conventional electronic and thermal expansion contributions. However, a comparison with the δ-phase demonstrates that most of the entropy stabilizing the δ-phase of plutonium at high temperature comes from unconventional sources, including electron correlations, intrinsic phonon softening, and possibly intrinsic localized modes. Interestingly, $4d \rightarrow 5f$ transitions in electron energy-loss spectroscopy show little difference in spin-orbit interaction of the $5f$ states between α- and δ-Pu [32, 33]. Further, DMFT calculations show only a modest change of ~0.2 electron occupation between α- and δ-Pu [27, 34]. This means that the crystal lattice dynamics of α- and δ-Pu are important in the large-volume transformation and, accordingly, more phonon measurements are needed to understand the unconventional entropic sources in δ-Pu and their role in the $\delta \rightarrow \alpha$ phase transformation.

Acknowledgements

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Figure Captions

Figure 1. Phonon density of states of pure α-Pu and δ–$Pu_{0.98}Ga_{0.02}$ measured at room temperature. The open circles were measured in this study, while the solid line was calculated from the force-constant-model fit to the measured dispersion curves by Wong *et al.* (2003), convoluted with the instrument resolution function. The α-phase phonon DOS is clearly stiffer than the δ-phase, which is expected given the higher density of monoclinic α-Pu.

Figure 2. Heat capacity of pure α-Pu plotted measured from 2 K to 300 K. Contributions from the phonon DOS (C_V^{ph}) volume expansion ($9Bv\alpha^2T$) and electronic excitations (γT) were calculated from measured data, as described in the text. For clarity error bars are shown on every fourth data point.

Figures

Figure 1

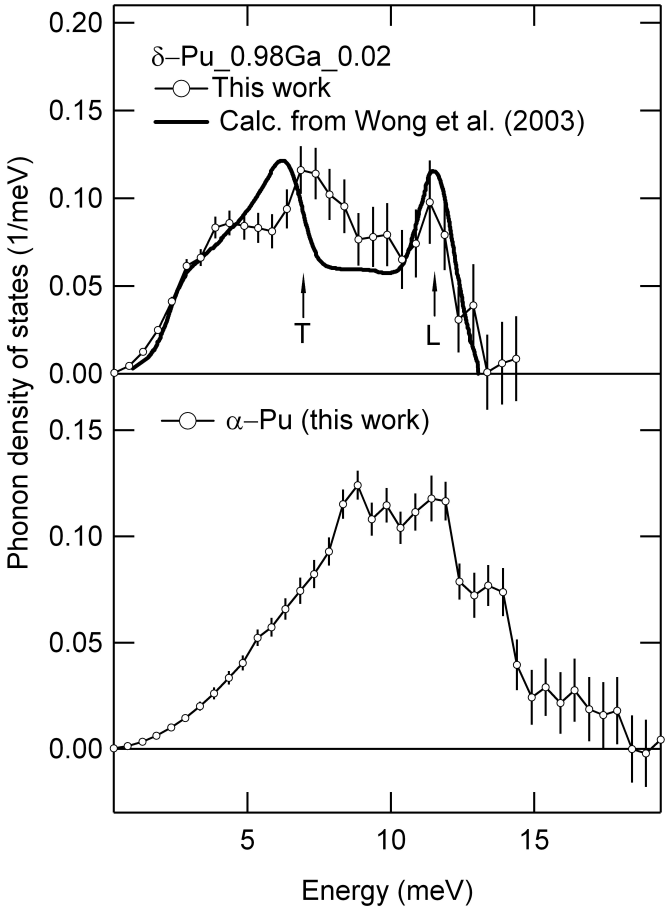
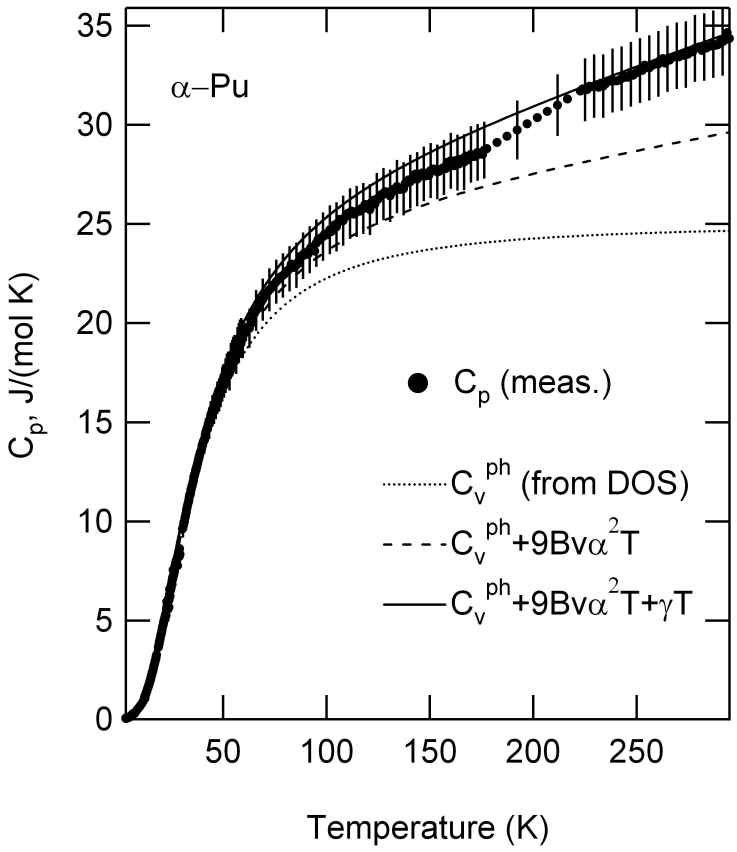


Figure 2


α–Pu
C_p (meas.)
C_v^{ph} (from DOS)
$C_v^{ph}+9Bv\alpha^2T$
$C_v^{ph}+9Bv\alpha^2T+\gamma T$
C_p, J/(mol K)
Temperature (K)
0
5
10
15
20
25
30
35
50
100
150
200
250